PCT/FR03/01013
10/509103

DT09 Rec'd PCT/PTO 27 SEP 2004

Steel block for the manufacture of moulds for the injection moulding of plastics material or for the manufacture of metal-working parts

The present invention relates to a steel block which may be used, in particular, for the manufacture of moulds for the injection moulding of plastics materials or for the moulding of metals such as light alloys or for the manufacture of metal-working tools.

Moulds for the injection moulding of plastics materials are generally produced from steels of which the hardness is approximately 300 HB. When these moulds are used for the moulding of plastics such as industrial plastics or thermosetting plastics, however, it is preferable to use harder steels which are more resistant to wear. A steel of the type 55 NCDV 7 containing about 0.55% of carbon, 1.75% of nickel, chromium, molybdenum and vanadium may therefore be used and allows the manufacture of moulds of which the hardness is approximately 400 HB. However, this steel has a plurality of drawbacks: it is difficult to machine and difficult to weld. In addition, this steel often has localised segregations which constitute hard points which are detrimental to polishing or to chemical graining. These two drawbacks are particularly undesirable because manufacture of the moulds necessitates significant machining and the moulds are generally repaired by reloading by welding and polished or grained. In addition, these moulds must be able to be surface-hardened, for example by nitriding, without losing their hardness.

For applications which are even more demanding and particularly if the injection-moulded plastics contain very rigid fibres, it is preferable to use steels which are even harder and more resistant to wear. Similarly, the increase in the injection moulding pressures has also led to a search for stronger and therefore harder steels. Finally, for certain applications involving the injection moulding of light alloys or cold or warm working of metals, the mechanical stresses imposed on the tools and the requirements of resistance to wear necessitate a steel having hardnesses higher than 450 HB. A steel having strength of approximately 450 or even 500 HB such as the grades AISI H11 or H13 which are also commonly used for the injection of light alloys may thus be required. These steels contain about 0.4% of carbon, 5% of chromium, 1.25% of molybdenum, 0.3 to 1% of vanadium. However, steels of this type have the same above-mentioned drawbacks as 55 NCDV 7, to a higher degree.

In addition, a further problem arises particularly crucially with the increase in hardness, which is almost inevitably accompanied by a reduction in toughness: the risk of fissuring between the cooling ducts and the surface of the mould impression, which these ducts should effectively cool by passing relatively close to this surface.

The object of the present invention is to overcome these drawbacks by proposing a steel for moulds or for the manufacture of parts for metal-working which is easier to weld and easier to machine, polish and grain and is a better conductor of heat than steels according to the prior art, and allowing the manufacture of parts or tools having a hardness of approximately 450 HB to more than 500 HB, even after

surface-hardening by nitriding, and this means that the required characteristics, in particular hardness characteristics, have to be compatible with tempering at at least 530°C.

The invention accordingly relates to a steel block having a thickness which is greater than 20 mm and may attain 1500 mm, of which the structure is martensitic or martensito-bainitic, of which the hardness is between about 430 HB and 520 HB at all points, for the manufacture of parts for moulds or for tools, the chemical composition of the steel comprising, in % by weight:

$0.180\% \leq C \leq 0.400\%$

$Si \leq 0.8\%$

$Mn \leq 2.5\%$

$Ni \leq 3\%$

$Cr \leq 3.5\%$

$Mo + W/2 \leq 2.8\%$

$V + Nb/2 + Ta/4 \leq 0.5\%$

$Al \leq 0.4\%$

$Ti + Zr/2 \leq 0.1\%$

- boron in a content of between 0.0005% and 0.015%,
- optionally one or more elements from among sulphur, selenium and tellurium, the sum of contents of these elements being less than or equal to 0.2%,
- optionally one or more elements from among lead and bismuth, the sum of contents of these elements being less than or equal to 0.2%,

- optionally calcium in a content less than or equal to 0.1%,

the remainder being iron and impurities resulting from production, the copper being an impurity, the chemical composition also satisfying the following equations:

$$3.2 \leq Tr \leq 9$$

$$85 \leq Dr \leq 95$$

$$U/Dr \leq 10.0$$

$$Mo^* + 3xV^* \geq 0.4\%$$

in which, for contents expressed in %:

$$Tr = 1.8xC + 1.1xMn + 0.7xNi + 0.6xCr + 1.6xMo^* + K$$

wherein K = 0 if the steel does not contain boron and K = 0.5 if the steel contains boron

$$Dr = 54xC^{0.25} + 24.5x(Mo^* + 3xV^*)^{0.30} + 1.58xMn + 0.74xNi + 1.8xSi + 12.5x(Cr)^{0.20}$$

$$U = 1600xC + 100x(0.25xCr + Mo^* + 4.5xV^*)$$

$$R = 3.8xC + 10xSi + 3.3xMn + 2.4xNi + 1.4x(Cr + Mo^*)$$

$$Mo^* = Mo + W/2$$

$$V^* = V + Nb/2 + Ta/4$$

and the contents of boron, aluminium, titanium, zirconium and nitrogen, expressed in thousandths of % by weight, are such that:

$$B \geq \frac{1}{3} \times K1 + 0.5$$

wherein $K1 = Min\ (I^*;J^*)$

$I^* = Max\ (O;I)$ and $J^* = Max\ (O;J)$

$I = Min(N;\ N-0.29(Ti+Zr/2-5))$

$$J = Min\left(N;0.5\left(N-0.52\,Al+\sqrt{(N-0.52\,Al)^2+283}\right)\right).$$

Preferably, the chemical composition is such that:

$R > 11$

Also preferably, the chemical composition is such that:

$R \leq 2.7xTr$

It is preferable that the silicon content remains strictly at 0.45 % by weight.

Preferably, the composition is such that: $R/(2.7xTr) \leq 0.90$, more preferably $R/(2.7xTr) \leq 0.80$.

Preferably, the composition is such that $U/Dr \leq 9.0$.

In addition, it is preferable that the chemical composition of the steel is such that:

$0.230\% \leq C \leq 0.350\%$

$Si \leq 0.30\%$

$0.1\% \leq Mn \leq 1.8\%$

$Ni \leq 2.5\%$

$0.2\% \leq Cr \leq 3\%$

$Mo + W/2 \leq 2.5\%$

$V + Nb/2 + Ta/4 \leq 0.3\%$

$Mo^* + 3xV^* \geq 0.8\%$

and even more preferable, such that:

$0.240\% \leq C \leq 0.320\%$

$Si \leq 0.15\%$

$0.1\% \leq Mn \leq 1.6\%$

$Ni \leq 2\%$

$0.2\% \leq Cr \leq 2.5\%$

$0.3\% \leq Mo + W/2 \leq 2.5\%$

$V + Nb/2 + Ta/4 \leq 0.3\%$

$Mo^* + 3xV^* \geq 1.2\%$

It is therefore preferable that the composition is such that $Tr > 4.5$.

The invention also relates to a mould part made of steel which is machined in a block according to the invention, of which at least a surface portion is hardened by nitriding and of which the hardness at all points is between 430 HB and 530 HB.

The steel according to the invention has the advantage of being a better conductor of heat than the steels according to the prior art. This better thermal conductivity allows the cooling ducts to be further removed from the surface of the moulds than when using steels according to the prior art. Thus, the risk of fissures between the ducts and the surface of the mould impression is substantially reduced. In addition, owing to the better thermal conductivity, the cooling of the

moulds takes place more uniformly and this improves the quality of moulding.

The steel according to the invention is also intended for the manufacture of metal working parts.

The invention will now be described in more detail and illustrated but not limited by examples.

The parts for moulds or for metal working are manufactured by machining solid blocks of steel which are quenched to obtain a homogeneous martensito-bainitic structure and tempered to obtain the desired properties of hardness and ductility. It is therefore necessary to use a steel having high temperability and significant hardenability. However, these hardened steels must have the best possible machinability and the highest possible thermal conductivity. This last property helps to improve the productivity of the moulding operations. The combination of these various properties is initially contradictory. In fact, it is known that, the harder the steel is, the easier it is to machine, and it is known that the machinability may be improved by adding alloying elements such as sulphur, calcium, selenium, tellurium or lead. However, these additions have to be limited in steels for moulds because, although they are acceptable when the surface of the mould impressions is grained, they are detrimental when the surfaces are polished. Whatever the case, these additions are inadequate. It is also known that the thermal conductivity and quenchability of steel vary inversely as a function of its composition. These requirements are therefore contradictory. However, the inventors have found, in a novel manner, that it is possible to find ranges of composition which result in

combinations of properties which are substantially better than those of known steels. These ranges of composition are defined, on the one hand, by spreads of contents in each of the elements of the composition and, on the other hand, by formulae which are to be adhered to.

To obtain these combinations of properties, the steel must contain:

- 0.18% to 0.4% of carbon to form carbides which harden without excessively impairing weldability, toughness and machinability, and this content must preferably be between 0.230% and 0.350% and more preferably between 0.240% and 0.320%;
- less than 0.8%, preferably less than 0.30% and more preferably less than 0.15% of silicon. This element which is generally used to deoxidise the steel during production adversely affects the thermal conductivity. However, it is always present at least in traces;
- less than 2.5% of manganese, preferably 0.1 to 1.8% and more preferably 0.1% to 1.6%, to obtain good quenchability without causing excessive segregation which would reduce the ability to obtain good surface states on the moulds. The element is always present, at least in the state of traces. In addition, it is preferable for its content to be higher than 0.1% in order to trap the sulphur which is still present in the state of impurities. If sulphur has been added to improve the machinability, the minimum manganese content must preferably be adapted accordingly and must be at least 5 times and preferably 7 times the sulphur content;

- less than 3% of nickel, preferably less than 2.5% and more preferably less than 2%. This element allows the quenchability to be increased but is very expensive. It may be present in traces. In applications requiring greater toughness and very uniform hardness, however, it may be worth reducing the manganese content in favour of the nickel in a proportion of two parts of nickel for one part of manganese. This substitution of 1 part of manganese by nickel also has the advantage of reducing segregation;
- less than 3.5% of chromium, preferably 0.2% to 3% of chromium and more preferably 0.2% to 2.5%. This element increases the quenchability but, in an excessive quantity, tends to enrich the carbides in chromium to the detriment of other more favourable elements such as molybdenum, tungsten, vanadium, niobium and tantalum. It may be present in traces;
- molybdenum and/or tungsten in contents which are such that the sum Mo* = Mo + W/2 is less than 2.8% and preferably less than 2.5%; it is also preferable that it is higher than 0.3%. These elements have a pronounced quenching effect. In addition, they substantially reduce process annealing, and this is desirable when the impressions of the moulds are subjected to surface treatments such as nitriding at temperatures of at least 500°C. In excessive quantities, however, they impair machinability;
- optionally at least one element selected from among vanadium, niobium and tantalum in contents which are such that the sum V* = V + Nb/2 + Ta/4 is less than 0.5% and preferably less than 0.3%. These elements increase the resistance to process annealing, in particular when

tempering is carried out above 550°C. They also increase the wear resistance of the mould impressions. In an excessive quantity, however, they impair machinability and weldability;

- 0.0005% to 0.015% of boron. This element substantially increases the quenchability without adversely affecting the thermal conductivity. In addition, as its effect disappears at the high austenitising temperatures encountered during welding, it is favourable to good repairability by welding. Below 0.0005%, which is practically the limit of detection by analysis means, it does not have a significant effect. Above 0.015% it embrittles the steel without increasing its quenchability;
- optionally up to 0.4% of aluminium and optionally one or more elements from among titanium and zirconium, wherein the sum Ti + Zr/2 may attain 0.1%. These elements are strong deoxidising agents. In addition, they fix the nitrogen which is still present at least as an impurity in contents generally of less than 0.0250% but possibly of even less, though if the steel contains boron, the nitrogen content must be less than 0.0250%. The presence of at least one element from among Al, Ti and Zr is desirable for the boron to be fully effective.

To enable the aluminium, titanium and zirconium, taken alone or in a combination of two or three of these elements, to protect the boron from the nitrogen and thus make it fully effective, the boron, aluminium, titanium, zirconium and nitrogen contents, expressed in thousandths of % by weight must be such that:

$$B \geq \frac{1}{3} \times K1 + 0.5$$

wherein $K1 = \mathrm{Min}\ (I^*;J^*)$

$I^* = \mathrm{Max}\ (O;I)$ and $J^* = \mathrm{Max}\ (O;J)$

$I = \mathrm{Min}(N;\ N-0.29(Ti+Zr/2-5))$

$$J = \mathrm{Min}\ \left(N;0.5\left(N - 0.52\,Al + \sqrt{(N - 0.52\,Al)^2 + 283}\right)\right).$$

- the copper may be in the form of traces or impurities, up to contents of approximately 0.3%;
- optionally one or more elements from among sulphur, selenium and tellurium in a small quantity, the sum of the contents of these elements having to be less than 0.200%. If the steel is intended for the manufacture of moulds having a polished, chemically grained surface, however, the sum of contents of these elements must be less than 0.025%, or preferably less than 0.005%;
- optionally one or more elements from among lead and bismuth, the sum of contents of these elements being less than 0.2%. If the steel is intended for the manufacture of moulds having a polished, chemically grained surface, however, it is preferable that the steel does not contain such elements;
- optionally calcium in a content of less than 0.100%. If the steel is intended for the manufacture of moulds having a polished, chemically grained surface, however, it is preferable that the steel does not contain this element because its positive action on machinability is achieved in conjunction with sulphur, of which the addition is preferably limited if the steel has to be polished or grained;

- the remainder of the composition consists of iron and impurities resulting from production. It must be noted that, in the case of all the alloying elements of which the minimum content is not imposed, if these elements are not added they may still be found at least in the form of residuals or impurities in very low contents.

Within the limits just defined, the composition of the steel must be selected in order to obtain the desired characteristics for use. For this purpose, the composition must be such that:

- the value Tr = 1.8xC + 1.1xMn + 0.7xNi + 0.6xCr + 1.6xMo* + K, wherein K = 0 if the steel does not contain born and K = 0.5 if the steel contains boron, in other words, if boron has been added in a content higher than or equal to 0.0005%, is higher than 3.2 and preferably higher than 4.5 to obtain adequate quenchability. In particular Tr must be higher than 4.5 for obtaining a martensito-bainitic structure without any traces of a perlitic structure on parts of which the thickness may exceed 1000 mm and be as high as 1500 mm;
- the value Dr = $54xC^{0.25}$ + $24.5x(Mo^* + 3xV^*)^{0.30}$ + 1.58xMn + 0.74xNi + 1.8xSi + $12.5x(Cr)^{0.20}$ must be between 85 and 95 in order to obtain adequate hardening by the carbides without excessively impairing machinability;
- the value U = 1600xC + 100x(0.25xCr + Mo* + 4.5xV*) which is an indicator of machinability (the lower U, the better the machinability) must be below 10.0 and preferably below 9.0;
- the value R = 3.8xC + 10xSi + 3.3xMn + 2.4xNi + 1.4x(Cr + Mo*) which varies with the thermal resistivity, in other

words the reverse of the thermal conductivity must preferably be less than 2.7xTr. More preferably, the ratio R/(2.7xTr) must be less than or equal to 0.90 and even more preferably less than or equal to 0.80. In view of all the requirements of characteristics desired for steel, however, this value may not generally drop below 11 also; the invention relates more particularly to steels in which R > 11, while being as low as possible;

- in view of all the stresses, the sum Mo* + 3xV* must be higher than 0.4%; if the composition of the steel corresponds to the preferred analysis:

$0.230\% \leq C \leq 0.350\%$

$Si \leq 0.30\%$

$0.1\% \leq Mn \leq 1.8\%$

$Ni \leq 25\%$

$0.2\% \leq Cr \leq 3\%$

$Mo + W/2 \leq 2.5\%$

$V + Nb/2 + Ta/4 \leq 0.3\%$

Mo* + 3xV* must be higher than 0.8%; if this steel corresponds to the more preferred analysis:

$0.240\% \leq C \leq 0.320\%$

$Si \leq 0.15\%$

$0.1\% \leq Mn \leq 1.6\%$

$Ni \leq 2\%$

$0.2\% \leq Cr \leq 2.5\%$

$0.3\% \leq Mo + W/2 \leq 2.5\%$

$V + Nb/2 + Ta/4 \leq 0.3\%$

Mo* + 3xV* must be higher than 1.2%.

To manufacture a mould with this steel, the steel is produced, is cast and hot-rolled or hot-forged in a known manner and cut to obtain blocks of which the thickness is greater than 20 mm and may exceed 100 mm and attain 400 mm, possibly 600 mm and even 1500 mm. It should be noted that, with the smallest thicknesses, the blocks may be sheets or large plates and, with the greatest thicknesses, they are generally forged blocks.

The blocks are austenitised, optionally in the forging or rolling heat, at a temperature higher than AC_3 and preferably lower than 950°C, in particular when the steel contains boron, and they are then quenched in air, oil or water, depending on the thickness and quenchability of the steel, so as to obtain a martensitic or martensito-bainitic structure in all the mass. Finally, they are tempered at a temperature higher than 500°C and preferably of at least 550°C but lower than AC_1. A hardness between approximately 430 HB and 530 HB is thus obtained.

In such blocks, parts of moulds comprising impressions which are polished and optionally grained are machined in a known manner. Optionally, these parts are surface hardened, for example by gaseous nitriding. After gaseous nitriding, apart from the extreme nitrided surface of the parts, the hardness of the steel is between approximately 430 HB and 530 HB.

By way of example and comparison, the analyses compiled in Table 1, of which certain characteristics are compiled in Table 2, are considered.

Examples 1 to 6, 9 to 12 and 14 to 16 correspond to the invention and examples 17, 18, 20 and 21 are given by way of comparison. These steels do not contain additions of selenium, tellurium, lead, bismuth or calcium. However, they contain a little sulphur, between 0.010% and 0.020%.

For all these steels, the hardness HB has also been determined in the tempered quenched state, in other words for a martensitic or martensito-bainitic structure tempered at 550°C, as well as the hardness HVHAZ in the heat-affected zone in the vicinity of a weld which has been compared with the hardness HVbasic of the basic metal not affected by the heat. These results are also compiled in Table 1.

These two tables show that, with a comparable hardness (HB) and comparable coefficient of hardness Dr, the steels according to the invention have better machinability (lower U/Dr ratio) than the steels given by way of comparison. In addition, they are better suited for repair by welding and, in particular, have a more uniform response to polishing after repair than the steels given by way of comparison since the hardness in HAZ is lower and, in particular, the HVHAZ to basic HV ratio is lower. In the steels according to the invention, the ratio of HVHAZ/HVbasic does not actually exceed 1.20 when the carbon is less than or equal to 0.35%.

Table 1

	C	Si	Mn	Ni	Cr	Mo	W	V	Nb	Cu	B*	Al*	Ti*	N*
1	0.25	0.15	1.3	0	2.1	1	0	0.3	0	0.2		25		6
2	0.24	0.13	1.2	0.3	2.5	1	0.9	0.26	0.1	0.2		4		8
3	0.2	0.1	1.3	1	2	1.1	0.8	0.3	0	0.2		19		4
4	0.25	0.15	1	0.2	2	2.1	0	0.3	0	0.3		35		5
5	0.28	0.15	1	0.2	3.3	1.8	1.5	0.3	0	0.2		22		5
6	0.29	0.04	1.2	1.2	2.1	1	0	0.16	0.28	0.02		27	12	6
9	0.35	0.15	0.7	1	1.3	1.5	0	0.28	0	0.3	2	65		5
10	0.35	0.15	1.4	1.5	1.5	1.5	0	0.28	0	0.2	2	14	22	6
11	0.28	0.12	0.7	1.2	2.2	1.6	0	0.2		0.3		18		3
12	0.31	0.12	0.2	1.2	2.2	1.6	0	0.2	0	0.1	3	32	18	5
14	0.38	0.13	1.3	0.2	2.9	1.5	0	0.1	0	0.2		21		9
15	0.39	0.05	1.3	1.8	2	1.55	0	0.09		0.2		27		2
16	0.39	0.03	1.3	1.5	3.2	0.8	0	0.1		0.2		25		3
17	0.39	0.3	0.63	0.1	1.5	0.45	0	0.42	0	0.1		18		4
18	0.38	1	0.4	0.2	5	1.25	0	0.34	0	0.1		22		5
20	0.34	0.25	0.8	0.2	0.5	0.5	0	0.6	0	0.3		12		7
21	0.39	0.45	0.57	0.1	3.2	0.7	0	0.24	0	0.2		15		5

* boron, nitrogen, titanium and aluminium are expressed in thousandths of %

Table 2

	Tr	Dr	U	R	R/2.7Tr	U/Dr	HB	HVHAZ	HVHAZ/HVbasic
1	4.74	84.7	688	11.1	0.87	8.12	440	542	1.12
2	5.78	86.9	731	12.4	0.8	8.41	460	540	1.07
3	6.09	85.3	655	13.4	0.81	7.68	443	500	1.03
4	6.25	88.6	795	12	0.71	8.97	472	539	1.04
5	7.8	92.7	921	14.5	0.69	9.93	515	588	1.04
6	5.54	86.7	752	12.7	0.85	8.67	460	586	1.16
9	5.78	88.4	869	11.5	0.73	9.82	477	626	1.19
10	7.02	90.3	874	15.3	0.8	9.67	493	641	1.18
11	5.99	87.2	753	12.8	0.79	8.64	462	574	1.13
12	6	87.4	801	11.2	0.69	9.17	462	597	1.18
14	6.39	89.5	876	13.7	0.79	9.78	485	679	1.27
15	7.07	89.8	870	15.6	0.82	9.68	493	685	1.26
16	6.38	86.9	829	15.3	0.89	9.54	455	701	1.4
17	3.09	86.6	896	9.53	1.14	10.3	460	663	1.31
18	6.26	93.6	1011	22	1.3	10.8	530	727	1.25
20	2.73	85.4	877	8.31	1.13	10.3	442	601	1.24
21	4.44	87.4	882	13.6	1.13	10.1	465	694	1.36

These steels are suitable for the manufacture of parts of moulds for the injection moulding of plastics materials. But they are also suitable for the manufacture of metal-working tool parts.